

Appl. No. 10/693,360
Response dated August 30, 2007
Reply to Final Action of May 11, 2007

REMARKS

Claims 1, 2, 9 and 17 remain as originally or previously presented. Claims 3, 13, 14 have previously been cancelled. Claims 4 – 7, 10 – 12, 15 – 20 remain withdrawn as they are directed to a non-elected invention. New claims 21 – 24 have been added.

Claims 1, 2, 8, 9, and 17 have been rejected under 35 USC §112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. The Examiner argues that the term “segmented copolyester” is not recognized in the art and is not defined in the specification, such that an artisan would not be appraised at the meaning of “segmented copolyesters” and thus would be unable to discern the metes and bounds of the claimed invention. However, this is not a case in which the Applicant is acting as his own lexicographer and must define what is meant by some novel term. As in the last response, Applicant asserts that the term “segmented” as applied to polymers is well known to those of ordinary skill in the art. Attached hereto, please find a copy of the first two pages of a thirty-year-old article from the Journal of Applied Polymer Science regarding an application for Hytrel®, a segmented polyether ester supplied by DuPont. Also attached is a copy of a page from the Concise Polymeric Materials Encyclopedia, published in 1998 by CRC, discussing segmented polyurethanes as blood compatible polymers in the penultimate paragraph of that page. Thus, it is asserted that there is no need to define what is included or excluded by the term “segmented copolyester” in order to define the metes and bounds of the invention. A person of ordinary skill in the art already knows what is meant by such term. Accordingly, it is submitted that the term

Appl. No. 10/693,360
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"segmented copolyester" is well known to those of ordinary skill in the art and it is requested that the Examiner reconsider and withdraw the present rejection.

Claims 1 and 2 have been rejected under 35 USC §102(b) as being unpatentable over Tian et al. In response to the Applicant's last response the Examiner argues that Applicant's allegation that the copolymers of Tian et al. would have a heat of fusion above 40 J/g to be mere speculation without evidentiary support. Accordingly, citations from the technical and patent literature to substantiate such statement are listed in the table, below. Copies of the appropriate sections of each reference are attached hereto.

Typical ΔH_f Values of High Lactide and High ϵ -Caprolactone Copolymers

Polymer Composite	ΔH_f , J/g	Reference
Segmented 88/12 <i>l</i> -Lactide/Trimethylene Carbonate Copolymer	62	Absorbable and Biodegradable Polymers (Shalaby & Burg, Eds.) CRC Press, Boca Raton, 2004, p. 20.
95/5 <i>l</i> -Lactide/ ϵ -Caprolactone Copolymer	67	Example 9 of U.S. Pat. No. 6,342,065
95/5 ϵ -Caprolactone/Glycolide Copolymer	67	Example 2 of U.S. Pat. No. 6,703,035
95/5 A Triaxial ϵ -Caprolactone/Glycolide Copolymer	66	Example 4 of U.S. Pat. No. 7,048,753

Accordingly, it is submitted that the Tian, et al. article does not anticipate the present claims and it is requested that the Examiner reconsider and withdraw the present rejection.

Claims 1 and 2 have been rejected under 35 USC §102(b) as being unpatentable over the Bennett, et al. article. In response to the Applicant's last response the Examiner argues that the present claims do not require the present segmented copolyesters to be non-liquid at room temperature. However, the present claims do require that the

segmented copolyesters have a molecular weight of at least 5 kDa. The Bennett et al. polymer has a molecular weight of 1249. Further, the molecular weight of the Bennett et al. polymer cannot be increased because it is subsequently end-capped with diisocyanate groups for a specific purpose. Even if the molecular weight with the end-capped groups is considered, it is well below the required molecular weight for the present segmented copolyesters. Accordingly, it is requested that the Examiner reconsider and withdraw the present rejection.

Claims 1 – 3 have been rejected under 35 USC §102(e) as being anticipated by U.S. Patent No. 7,097,907 to Bennett, et al. However, the polymers disclosed in that reference are either low molecular weight polymers useful as bone putty, similar to those disclosed in the Bennett article, discussed above, or are higher molecular weight, soft, non-crystalline polymers useful as fiber coatings or bone wax. The present crystalline polymers would not be appropriate for use in any of these applications. Similarly, the Bennett, et al. polymers cannot be employed as sealants for vascular devices as are the present claimed polymers. By definition, sealants must block flow. The soft polymers of the Bennett, et al. patent cannot perform this task. Accordingly, it is requested that the Examiner reconsider and withdraw the present rejection.

Claims 8, 9, and 17 have been rejected under 35 USC §103(a) as being unpatentable over Tian in view of U.S. Patent No. 6,309,669 to Setterstrom, et al. The Examiner argues that the Tian reference only lacks carboxylate side-groups which are taught by Setterstrom, et al. However, as discussed above, one of ordinary skill in the art would recognize that the present polymers, which have a limited degree of crystallinity as

Appl. No. 10/693,360
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measured in terms of the heat of fusion (ΔH_f) at less than 25 J/g, as is set forth in claim 1, are more highly compliant (flexible) than those of Tian, which contain highly crystallizable PCL and PLL blocks. End-capping the polymer of Tian as is taught by Setterstrom, would not render obvious the present highly compliant, segmented copolyesters. Accordingly, it is requested that the Examiner reconsider and withdraw the present rejection.

Claims 8, 9, and 17 have been rejected under 35 USC §103(a) as being unpatentable over the '907 reference in view of Setterstrom, et al. Hereagain, the Examiner argues that the '907 reference only lacks carboxylate side-groups which are taught by Setterstrom, et al. However, as discussed above, the polymers of the '907 reference cannot be used as sealants. End-capping the polymers of the '907 reference as is taught by Setterstrom, et al., would not render those polymers crystalline. Accordingly, it is requested that the Examiner reconsider and withdraw the present rejection.


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The prior art made of record and not relied upon has been carefully considered and has been deemed to be of no more relevance than that relied upon.

Accordingly, it is submitted that the present case is in condition for allowance and such action is respectfully requested.

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Polymeric Systems for Acoustic Damping. I. Poly(vinyl Chloride)-Segmented Polyether Ester Blends

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Synopsis

A series of six Hytrel/PVC blends were prepared by solution blending Hytrel in methylene chloride and PVC in tetrahydrofuran. The samples were subsequently prepared in sheet form by hot pressing at 170°C. Physical and mechanical properties of the homopolymers and the blends were investigated. The copolyester homopolymer is a partly crystalline elastomeric material. The level of crystallinity was measured by x-ray diffraction and the sensitivity of this level to heat treatments and quenching determined by DSC. A Morgan pulse propagation meter was used to measure sonic velocity and, indirectly, acoustic impedance of the blends. Dynamic mechanical studies indicated that blends containing 25%-60% by weight of Hytrel were completely compatible in the sense that a single glass transition was observed; but as the Hytrel level was increased to 60% and 65%, a shoulder became apparent on the low-temperature side of the glass transition peak. At 80% Hytrel, two peaks were observed, indicating incompatibility. The glass transition temperatures of these blends were found to decrease linearly with added Hytrel.

INTRODUCTION

This paper is the first of a series of reports on investigations into the use of a variety of polymeric systems as possible acoustic damping materials. The increased awareness of noise as a health hazard is leading to the search for more effective noise attenuation systems. A considerable amount of noise originates in machinery because of the inherently very low damping character of metals. The physical properties of a material which influences its sound insulation performance are stiffness, surface mass, and damping characteristics.¹

As far as polymers are concerned, it is likely that systems having high damping will not have particularly high moduli. If stiffness becomes an important factor in any given sound insulation application, it is possible to use constrained layer damping^{2,3} where the polymeric damping material is trapped between stiff outer skins such as metal sheet. The surface mass of polymeric damping materials may be enhanced by the incorporation of dense fillers such as barytes or lead, but this will result in a reduction in the maximum level of damping.

This and future work will be concerned primarily with the search for materials exhibiting high damping in the appropriate frequency/temperature range. The acoustic spectrum is generally regarded as extending from 20 Hz to 20 kHz, so it is necessary to have as large and as broad a relaxation dispersion over as much of this frequency range as possible.

3099

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3100

HOURSTON AND HUGHES

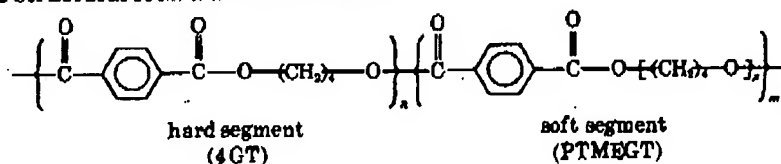
The most commonly used damping materials in acoustic and mechanical energy absorption are homopolymers and copolymers^{4,5} having a glass transition in the appropriate region. Such damping peaks are generally rather narrow, covering a temperature range of about 30°C for a given frequency in the acoustic range. Polymer blends of varying degrees of compatibility have also been investigated^{6,7} and generally lead to a broader loss mechanism than is the case for homopolymers and copolymers alone. Recent work by Sperling and co-workers^{8,9} into loss mechanism broadening in interpenetrating polymer network systems has resulted in interesting acoustic damping materials.

In this paper, we are largely concerned with compatible blends of poly(vinyl chloride) (PVC) and a relatively new commercial (du Pont) segmented polyether ester copolymer.¹⁰⁻¹³ Nishi, Kwei, and Wang¹⁴ and Kwei and Nishi¹⁵ have reported on certain mechanical properties of this system including the influence of heat treatments.

EXPERIMENTAL

Polymers

Hytrel. This segmented polyether ester (grade 4055) was kindly supplied by the E. I. du Pont de Nemours Company and had been prepared by melt transesterification of dimethyl terephthalate, poly(tetramethylene ether) glycol, and 1,4-butanediol. The product is a random block copolymer of crystallizable tetramethylene terephthalate (4GT), which forms the hard segments, and poly(tetramethylene ether) glycol terephthalate, which forms the soft segments. The structural formula is shown below:



Poly(vinyl Chloride). A rigid poly(vinyl chloride), Corvic (D60/11), containing no plasticizer was used.

The characterization data for both polymers are shown in Table I.

Preparation of Samples

Six Hytrel/PVC blends were prepared by solution blending where the Hytrel in methylene chloride and the PVC in tetrahydrofuran were mixed and the

TABLE I
Characterization Data for the Poly(vinyl Chloride) and Hytrel Samples
Used in the Preparation of the Blends

	Poly(vinyl chloride)	Hytrel
$\bar{M}_n \times 10^{-3}$	80	30
\bar{M}_w/\bar{M}_n^a	—	1.56
Density, g/cm ^{3b}	1.415	1.152

^a By GPC.

^b 23°C.

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BLOOD COMPATIBLE POLYMERS 163

Blocked Polyurethane Copolymers

See: Polyurethanes, Blocked Copolymer (Reactive Modifiers for Epoxy Resins)

Blood

See: Blood Compatible Polymers
Blood Substitutes
Cell Separation Materials
Red Blood Cell Substitutes, Artificial (for Transfusion)

BLOOD COMPATIBLE POLYMERS

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Polymer materials are extending their applications to biomedical uses. In addition to packaging for medical devices and instruments, polymers are widely used as medical devices and instruments, artificial organs and implants, and in drug formulations and delivery systems. Such materials are called biomaterials and are categorized as metals, ceramics, polymers, or composites.

Practical polymer applications include artificial kidneys, membrane oxygenators, and blood vessels. When polymers are used in medical devices contacting blood, coagulation is a serious problem. The blood compatibility of polymers differs depending on their chemical composition and morphology. Despite an enormous amount of research, blood-compatible polymers are still a long way off. That is because the mechanism of thrombus formation is too complicated to find correlations between blood compatibility and material structure.

BLOOD-MATERIAL INTERACTION**Rationale: Antithrombogenicity Vs. Pseudointima**

There have been many approaches to preventing or decreasing activation of the thrombogenic pathways by tailoring the physicochemical properties of the polymer either to minimize thrombus formation or to selectively adsorb a passivating albumin layer. These approaches include smooth surfaces, hydrophilic surfaces, microdomain structures, inert surfaces, and incorporation of negative ions. In addition, pharmacologically active agents may be incorporated into the polymer to yield a slow-release system or immobilized onto a surface. From these researches we have made great progress in producing chronically nonthrombogenic cardiovascular devices. However, it appears to be impossible to produce long-lasting, completely nonthrombogenic material. Therefore, the other approaches consist of using rough surfaces, such as veins, flocked, or integrally textured surfaces, to encourage the formation of a living biological lining derived from blood itself.

BLOOD COMPATIBILITY OF POLYMERS**Medical Polymers**

Blood compatibility is one of the most important properties of biomedical polymers. In general, blood-compatible polymers should possess two characteristics: they should not induce

thrombus formation, immune response, inflammatory reaction, or infection; and they must be nontoxic, noncarcinogenic, and nonmutagenic.¹ Despite the several *in vitro* and *ex vivo/in vivo* methods reported, there is no standard method for evaluating blood compatibility.

Many polymers from natural rubber and cellulose to synthetic elastomers, polyurethanes (PUs), and hydrogel have been used in biomedical applications ranging from disposable syringes to materials for artificial organs.² Polymers currently being used are categorized according to their characteristics and end-use applications as follows: synthetic nondegradable polymers that were used in most long-term implantable devices and disposables, biodegradable or soluble polymers that were used as temporary scaffolding and barrier and drug delivery matrices, and experimental polymers.³

Cardiovascular Application of Polymers

Blood compatibility is of primary importance for those polymers that interact with blood. The polymers used in cardiovascular systems such as blood-contacting devices include a wide variety of commercial materials. There are three kinds of cardiovascular applications:⁴ replacements that are permanently implanted in the circulatory system (e.g., artificial hearts, heart valves, and vascular grafts); devices that are inserted into a blood vessel for varying periods of time (e.g., catheters, sensors, fibroscopes, and other imaging agents); and extracorporeal devices that remove and return blood from the body (e.g., blood oxygenators, hemodialysis units (so-called artificial kidneys), cardiopulmonary bypass, and liver perfusion systems).

DESIGN OF BLOOD-COMPATIBLE POLYMERS

Current approaches to blood-compatible polymers can be divided into three categories: new polymer synthesis, surface modification of existing polymers, and biological approaches.

Tailoring New Polymers

One approach to minimizing thrombus formation is to synthesize nonthrombogenic polymers. These nonthrombogenic polymers prevent activation of the thrombogenic pathway by tailoring the polymer surface to minimize blood interaction.⁵

For many years, microdomain-structured polymers have received much attention for their improved blood compatibility. Several research groups have synthesized and evaluated polymers with microheterogeneous surfaces. Okano et al.^{6,7} and Shimada et al.⁸ reported that block copolymers having hydrophilic-hydrophobic microdomain structures show antithrombogenicity both *in vivo* and *ex vivo/in vivo*.

Other polymer systems with microdomain structure include segmented polyurethanes (SPUs), which are widely used for medical applications because of their excellent physical and mechanical properties and relatively good blood compatibility. SPUs are segmented heterophase elastomers that exhibit a variety of physical and chemical properties depending on their synthetic conditions.

The surface modification of polymeric materials has been recently reviewed by Ikada.¹⁰

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TABLE 2.3

Chemical Composition and Physical Properties^a of Typical High Lactide-Based Polymers

Polymer Number	Polymer Composition ^b		DSC Data	
	L/TMC/CL	I.V. (dL/g)	T _m (°C)	ΔH _t (J/g)
V	88/12/0	3.27	183	62
VI	88/12/0	1.87	183	59
VII	88/8/4	2.46	180	50
VIII	86/15/0	2.97	170	53

^a All polymers were insoluble in hexafluoro-2-propanol for viscosity measurement.

^b Ratio of contributing components to segmented chains: L = *l*-lactide; TMC = trimethylene carbonate; CL = ε-caprolactone.

lactide content for the production of multifilament yarn and braided sutures therefrom.¹¹ Accordingly, highly crystalline copolymers were prepared using 86 to 88 M% of *l*-lactide and 12 to 14 M% of TMC or a mixture of TMC and CL. The polymers were made as described for similar polymers in Section 2.3.1. The composition and properties of four typical examples of these polymers (V to VIII) are summarized in Table 2.3. Conversion of the polymer to spun-drawn multifilament yarn was accomplished using a 3/4 in. single-screw extruder equipped with a multihole die and integrated with a spin-finish applicator, a take-up roll, heated and unheated Godeys, and winder. The multifilament yarns were prepared for braiding using an 8- or 16-carrier braiding unit. Accordingly, braids BR-I to BR-IV based on polymers V to VIII were constructed into clinically relevant sizes for use in orthopedic applications. Prior to testing, the spin-finish was removed, braid dimensions were stabilized, and an absorbable coating was applied. For coating, a nitrogenous caprolactone copolymer was used.¹² The tensile properties of the yarn and braid were determined using an MTS Minibionix Universal Testing Unit (Model 858). The *in vitro* BSR was evaluated using a phosphate buffered solution at pH 7.4 and a temperature of 37°C or 50°C. Braid properties and *in vitro* BSR data are summarized in Table 2.4.

The results of polymers V to VIII in Table 2.3 demonstrate that highly crystalline segmented copolymers of *l*-lactide can be produced using a solid-state polymerization protocol. The data from Braids BR-I to BR-IV in Table 2.4 show that these polymers are promising precursors for strong, multifilament yarn that can be converted into high-strength braids with exceptionally high knot strength. The high knot strength of this suture, as compared to Panacryl[®], is attributed to the inherent toughness of the yarn that, in turn, is associated with the unique segmented structure of the polymer chains. The results also reflect the promising properties of this braid for use not only in orthopedic applications but also for a broad range of surgical procedures.

Results in this study demonstrated the feasibility of designing segmented, high-lactide copolymer chains as crystalline fiber-forming polymers for the